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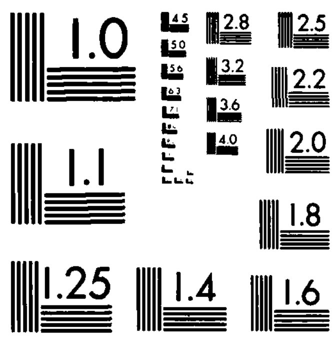

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Application of Conductive Polymer Technology to the Production of a Novel Multilayer Capacitor

by

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Abstract

Multilayer ceramic capacitors, due to their large capacitance, reduced volume and low cost, have become one of the fastest growing technologies in electronic devices. Present technology uses barium titanate as the dielectric which requires the use of precious metal (Pd, Pt, Au) internal electrodes as a result of the high firing temperatures (1300-1400°C). These precious metals are responsible for 50 to 60% of the total cost of the capacitor and are subject to strategic foreign disruption. It is the goal of this investigation to evaluate the feasibility of using a polymer based dielectric and a polymer thick film metal electrode to build a multilayer capacitor that would elimate the need for precious metals. Once this is accomplished, the next phase would ultimately involve the replacement of the silver in the polymer thick film electrode with synthetic metals.

The work involved an extensive literature review, discussions with researchers active in this field and the testing of prototype polymer capacitors. Evaluations were carried out based on capacitance, permittivity dissipation factor and short-term stability. The initial results were considered encouraging and a continuing effort in this direction is most feasible.

Introduction

As a result of their high volumetric efficiency and resultant small size, multilayer ceramic capacitors are an integral part of the electronics industry. The most widely used material in present technology is barium titanate. The firing temperature of this dielectric material is in the range of 1300°C to 1400°C. Since the conductive layer is also subjected to this high temperature, precious metals such as palladium, platinum and gold must be used. By doping the barium titanate with additives, the firing temperature can be reduced to approximately 1050°C at which point a silver-palledium electrode can be used. No polymer conductor can withstand such a high temperature.

Capacitance is the property of two or more conductors separated by a dielectric, which permits it to store electrical charge.[1] To give the maximum capacitance per unit area, the capacitor must have as high a dielectric constant as possible. The dielectric constant can be defined as the ratio of the capacity of a given electrode configuration including a specific dielectric to the capacitance of the same electrode system in a vacuum.[2] A dielectric will eventually break down under an increasing field. The value of this field in volts per thickness is defined as the dielectric strength. This breakdown is the result of either a thermal or electronic catastrophe.[3] Energy losses occur in the dielectric layer as a result of the migration, vibration and deformation of ions. It is very important to keep this loss factor at a minimum because it heats up the dielectric, decreases capacitance, and may cause total breakdown

if the losses ae too great.[4]

It is the intent of this investigation to evaluate the feasibility of using a polymer based dielectric and polymer thick film metal electrodes to build a multilayer capacitor. If this study shows technical feasibility, then the next step is to ultimately replace the polymer thick film metal electrodes with a synthetic metal conductor. This product, if successfully developed, could reduce the production cost of multilayer capacitors by over 50% and reduce dependence on strategic materials such as palladium, platinum and gold.

Procedure

The initial step of Phase I was to conduct an extensive literature search into capacitor technology and electronic materials. The search included outside sources of assistance through The Pennsylvania Technical Assistance Program (PENNTAP) and Advanced Technology Center of Southeastern Pennsylvania, as well as personal searches at several university libraries and the Philadelphia Public Library. A great deal of assistance and encouragement came from consulting with researchers in the field of electronics. A list of the consultants is given below.

1.	Dr. Leslie Eric Cross	Penn St. University
2.	Dr. Jim Biggers	Penn St. university
3.	Dr. Karl Norian	Lehigh University
4.	Dr. Devin Scoles	Drexel University
5.	Dr. William Eckert	TAM Industries
6.	Lew Hoffman	Hoffman Assoc.
7.	Al Zelinski	Metech, Inc.
8.	Dr. Brian Newman	Rutgers University

After reviewing the information gathered, the preliminary design and material selection were established. The first phase was to develop a potential dielectric material. Two polymers were initially chosen for testing; (1) polimide and (2) phenolic. They were chosen for their ability to withstand higher temperatures, ease of handling, low loss and high dielectric strength. Various dielectric powders were dissolved in each polymer resin. The list of dielectric powders includes:

1. Alumina
2. Two types of $BaTio_3$
3. Mica
4. Niobium
5. Silica
6. Tantalum
7. Tantalum pentoxide
8. Titanium dioxide

The second phase involved the development of potential electrode inks using a polymer thick film or synthetic metal inks. Table I shows the polymer thick film inks that were used.

	Material	Weight %	Use
1.	Polyimide Resin Silver Flakes	24.5 68.5	Used with polyimide based dielectrics.
2.	Epoxy Resin Silver Flakes	25.3 68.2	Used with all phenolic based dielectrics

Table I: The Composition of Each Polymer Thick Film Conductor Is Given

The ultimate goal of this project is to replace the precious metal electrodes now used in multilayer capacitor production with synthetic metal electrodes. To achieve this goal a functional polymer based dielectric system must be developed. Once a polymer dielectric and

polymer silver conductor based multilayer can be determined to be feasible more extensive research can be recommended to replace the polymer silver conductor with a synthetic metal electrode and ultimately produce a multilayer capacitor that is completely free of any precious metals.

One substrate material and one set of stainless steel screens for printing were used throughout the experiments to reduce the number of possible parameters. An alumina substrate was chosen to achieve a uniform and continuous print with good adhesion properties. The dielectric screen was 200 mesh with an emulsion thickness of .9 mils. The conductor screen was 230 mesh with an emulsion thickness of .9 mils. The inks were prepared by milling on a standard three roll mill.

Consultations with several manufacturers of multilayer ceramic capacitors were undertaken with the intent of learning the entire manufacturing process. Once this was understood polymer capacitors could be produced under similar conditions using silk screening methods. The samples were tested at Lehigh University under the supervision of Dr. Karl Norian. The initial tests measured capacitance, permittivity, dissipation factor and dielectric strength.

Results and Discussion

Polymers possess a dielectric constant in the range of only 2 to 10.[5] Using a 100% polymer dielectric, only a low permittivity material can be achieved. Present technology uses the polymer dielectric as an overglaze or protective coating on electronic devices.[6] Ceramics possess a much higher dielectric constant than polymers but their energy

losses are greater. A ceramic dielectric can't be used with a polymer thick film metal electrode due to the extreme differences in firing temperatures. Therefore, it is feasible that a dielectric composition containing both a polymer resin and a ceramic powder will offer a higher capacitance than a polymer dielectric and a lower loss factor than a ceramic dielectric. Thus, much of the work carried out in this investigation dealt with intercalating the polymer resin with a ceramic powder to build a dielectric that was compatible with the polymer thick film electrodes. These electrodes contain approximately 60 to 70% silver. If the Phase II Proposal is granted, the silver will be ultimately replaced by synthetic metals to further reduce the material costs of the multilayer capacitor.

The capacitance and dissipation factor were measured to determine each materials potential as a dielectric. The most promising results are given in Table II. The table includes the materials, weight percents, capacitance range, dielectric constant (K) range and dissipation factor. The units for capacitance are pico farads.

Table II

Composition	Material	Weight%	Capacitance Range	K-Range	Dissipation Factor
C-14	$BaTio_3$ phenolic - 1	68.3 27.7	1382 - 1550	28.7 - 51.2	.013 - .014
C-30	$BaTio_3$ phenolic - 2	73.7 26.3	935 - 1142	23.6 - 50.0	.005 - .006
C-32	$BaTio_3$ phenolic - 1	68.8 31.2	1208 - 1309	31.5 - 42.1	.006 - .007
C-39	$BaTio_3$ phenolic - 1	73.0 27.0	1222 - 1431	27.0 - 43.0	.010 - .016
C-7	$BaTio_3$ polyimide	51.5 36.2	521 - 862	16.5 - 39.0	.008 - .020
C-8	TiO_2 phenolic - 1	56.0 37.2	962 - 1090	22.0 - 29.3	.010 - .014
C-16	Ta phenolic - 1	63.7 30.3	781 - 1503	12.6 - 41.0	.050 - .260
C-9	TiO_2 phenolic - 2	57.0 38.0	537 - 745	14.2 - 25.2	.009 - .010

The highest capacitance values came from using barium titanate as the dielectric powder. In phenolic composition C-14, capacitance values were observed in the range of 1382 to 1550 pF. Other promising results came from using tantalum and titanium dioxide. Tantalum had capacitance values as high as 1503 pF in phenolic composition C-16. Capacitance values in the range of 962 to 1090 pF were achieved using titanium dioxide in phenolic composition C-8.

Tantalum pentoxide, alumina and silica gave discouraging results. The tantalum pentoxide had capacitance values only as high as 743 pF and a dissipation factor, 7.5%. Alumina and silica never reached 250 pF. Niobium and mica failed to store any charge in either a polyimide or phenolic resin.

In Table II, seven out of the eight compositions had acceptable dissipation factor values. Only composition C-16 with tantalum had values (5-25%) greater than 4%. Composition C-30 with barium titanate had a dissipation factor of only .005-.006 and a dielectric constant as high as 50.0.

Overall, phenolic had higher capacitance values than polyimide when the same dielectric powder was used. This can be seen with polyimide (862 pF) composition C-7 and phenolic (1189 pF) composition C-38 where the weight percent of barium titanate is 51.5% and 41.2%, respectively. The polyimide has a higher curing temperature, lower dissipation factor and greater resistance to chemicals and the environment. The phenolic offers greater ease of handling and higher doping percentages. Perhaps, future work could combine the two polymers into one system.

Phenolic -1 displayed higher capacitance values and a higher dissipation factor than phenolic - 2. In Table II, this can be seen with TiO_2 compositions C-8 and C-9 and $BaTiO_3$ compositions C-14 and C-30.

There are many possible parameters that affect the capacitance of the dielectrics. The capacitance, C, of a dielectric can be defined as $C = \frac{KA}{t}$ where K is the dielectric, A is the area and t is the film thickness of the dielectric. The capacitance can be increased by either increasing the dielectric constant or the area, or by decreasing the film thickness.[7] The dielectric constant is solely dependent on the material and can only vary by changing the formulations of the material. As a result of loading additional ceramic powder into the polymer, the dielectric constant will increase. This is shown in compositions C-38 and C-39 where the weight percents of barium titanate are 41.2% and73.0%, respectively. Composition C-39 had dielectric constant values in the range 27.0 to 43.0 compared with values of 17.1 to 30.1 for composition C-38.

The electronic component industry has achieved much success in size reduction of electronic devices. For this reason, increasing the area of the capacitor to increase the capacitance is not practical. However, reducing the film thickness is most desired. The limitations of our silk screening machines put a lower limit of approximately 10-12 microns after firing. Two dielectric layers are needed to avoid shorting out. Therefore, the dielectric layer can only be reduced to 20-24 microns. It is believed that an overall film thickness less than 12.5 microns is necessary to achieve the same results as a ceramic

capacitor.[8] Future work should be done in investigating various applications to achieve a thinner dielectric. Two possible alternatives are spinning and spraying. The paint industry has become quite successful in achieving a uniform, thin coating. The possibilities of achieving the same advantages through this process for the polymer dielectric is quite high.[9]

The particle size of the ceramic powder will affect the capacitance. In general, a reduction in particle size will cause an increase in capacitance. Therefore, the smallest available particle size was obtained for each sample. All the powders passed through a 325 mesh sieve.

A new "cement" type ceramic that cures by dehydration and therefore requires no firing was also evaluated. After investigating the idea with Dr. Eric Cross, Penn State University, it was determined that the new type of ceramic was not practical for capacitor work. The cement has a very porous structure much like plaster of paris. The pores would short out the dielectric and cause conductivity. The structure of the "cement" ceramic is uniaxial. Capacitance will only occur if the electronic field is applied along the same axis.

Conclusion

This investigation was conducted as a feasibility study with limited actual testing. Three out of the eight dielectric powders gave favorable results. The capacitance values for seventeen compositions exceeded the original proposal's goal of 300 pico farads. The highest capacitance values were in the range of 1382 to 1550 pF. It exhibited a dissipation

factor of .013. The composition contained 68.3% barium titanate and 27.7% phenolic. A similiar composition had capacitance values of 1300 pF and a dissipation factor of only .005. Further improvement should be achieved through increased loading of the powder, a more uniform particle dispersion and thinner film thickness. Thus, the need to develop alternative procedures to the conventional screen printing is necessary. One of several approaches would be to utilize the spraying techniques the paint industry. The application would enhance the possibilities of achieving a thinner more uniform film with a greater powder content.

In conclusion, the feasibility of using a polymer based dielectric and polymer thick film electrodes to build a multilayer capacitor has been demonstrated. It is believed that more extensive research in this area, concentrating on synthetic metal electrode should be undertaken.

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